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Optical and magnetic resonance studies of Mg-doped GaN homoepitaxial layers grown by molecular beam epitaxy

E.R. Glaser[a,*], M. Murthy[b], J.A. Freitas Jr[a], D.F. Storm[a], L. Zhou[c], D.J. Smith[c]

[a]Naval Research Laboratory, Washington, DC 20375-5347, USA
[b]Department of ECE, George Mason University, Fairfax, VA 22030, USA
[c]Center for Solid State Science, Arizona State University, Tempe, AZ 85287, USA

Abstract

Low-temperature photoluminescence (PL) and optically detected magnetic resonance (ODMR) at 24 GHz have been performed on a series of MBE-grown Mg-doped (10^{17}–$10^{20}\,cm^{-3}$) GaN homoepitaxial layers. High-resolution PL at 5 K revealed intense bandedge emission with narrow linewidths (0.2–0.4 meV) attributed to annihilation of excitons bound to shallow Mg acceptors. In contrast to many previous reports for GaN heteroepitaxial layers doped with [Mg] $> 3\times10^{18}\,cm^{-3}$, the only visible PL observed was strong shallow donor–shallow acceptor recombination with zero phonon line at 3.27 eV. Most notably, ODMR on this emission from a sample doped with [Mg] of $1\times10^{17}\,cm^{-3}$ revealed the first evidence for the highly anisotropic g-tensor ($g_{\parallel}\sim2.19$, $g_{\perp}\sim0$) expected for Mg shallow acceptors in wurtzite GaN. This result is attributed to the much reduced dislocation densities ($\leqslant 5\times10^{6}\,cm^{-3}$) and Mg impurity concentrations compared to those characteristic of the more conventional investigated Mg-doped GaN heteroepitaxial layers.
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1. Introduction

The nature and properties of Mg shallow acceptors and Mg-related or -induced deep centers in the III–V nitrides have been subjects of much experimental and theoretical investigation during the last 15 years. Most of this research has focused on highly Mg-doped ($\sim10^{18}$–$10^{20}\,cm^{-3}$) GaN layers grown on non-native substrates, such as sapphire and SiC, characterized by high dislocation densities ($\sim$mid-10^{8}–$10^{10}\,cm^{-2}$) that result from differences in the lattice constants and thermal expansion coefficients of the respective nitride films and underlying host substrates. In particular, many photoluminescence (PL) studies of Mg-doped heteroepitaxial GaN have revealed a variety of near-infrared and visible emission bands, including a so-called "red" PL band near 1.8 eV, broad "blue" PL bands with peak energy between 2.8 and 3.2 eV and a PL band at 3.27 eV with resolved LO phonon replicas attributed to recombination between residual shallow donors (SD) and Mg shallow acceptors (SA) [1]. In addition, both electron paramagnetic resonance (EPR) and optically detected magnetic resonance (ODMR) techniques have been employed to identify residual defects and gain more information on the nature of the Mg-related states [2,3]. One of the puzzling aspects common to all the magnetic resonance work was the nearly isotropic g-tensor (i.e., $g_{\parallel}$, $g_{\perp}\sim2$) found for the Mg SA in the highly dislocated and highly Mg-doped GaN layers.

In this work, combined PL and ODMR experiments have been performed on a set of Mg-doped (10^{17}–$10^{20}\,cm^{-3}$) GaN layers deposited by molecular beam epitaxy (MBE) on thick, free-standing GaN substrates characterized by threading dislocation densities less than $5\times10^{6}\,cm^{-2}$. In contrast to previous work, this study allowed us to separate the impact of high dislocation densities from effects due to high Mg-doping levels on the optical and spin properties associated with still the most important dopant employed today for making p-type GaN. Most notably, ODMR on the 3.27 eV SD–SA PL band from a GaN homoepitaxial layer with [Mg] of $\sim1\times10^{17}\,cm^{-3}$ provided the first observation of the highly

*Corresponding author. Tel.: +1 202 404 4521; fax: +1 202 767 1165.
E-mail address: glaser@nrl.navy.mil (E.R. Glaser).

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14. ABSTRACT
Low-temperature photoluminescence (PL) and optically detected magnetic resonance (ODMR) at 24GHz have been performed on a series of MBE-grown Mg-doped (1017?1020 cm 3) GaN homoepitaxial layers. High-resolution PL at 5K revealed intense bandedge emission with narrow linewidths (0.2?0.4 meV) attributed to annihilation of excitons bound to shallow Mg acceptors. In contrast to many previous reports for GaN heteroepitaxial layers doped with [Mg]43 1018 cm 3, the only visible PL observed was strong shallow donor?shallow acceptor recombination with zero phonon line at 3.27 eV. Most notably, ODMR on this emission from a sample doped with [Mg] of 1 1017 cm 3 revealed the first evidence for the highly anisotropic g-tensor (gJ 2.19, g? 0) expected for Mg shallow acceptors in wurtzite GaN. This result is attributed to the much reduced dislocation densities (p5 106 cm 3) and Mg impurity concentrations compared to those characteristic of the more conventional investigated Mg-doped GaN heteroepitaxial layers.

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anisotropic g-tensor (i.e., $g_{\|}\sim 2$–4, $g_{\perp}\sim 0$) expected for Mg SA based on $k\cdot p$ theory and the ordering of the valence band states in wz-GaN [4].

2. Experimental details

The PL and ODMR were performed on several Mg-doped GaN homoepitaxial layers (0.5–0.7 μm thick) deposited by MBE on Fe-doped, free-standing GaN substrates ($\sim$1 cm × 1 cm, 500 μm thick) grown by HVPE [5]. The GaN films were intentionally doped with Mg from 10^{17} to $10^{20}\,cm^{-3}$ as confirmed by secondary ion mass spectroscopy (SIMS) [6]. An undoped reference GaN homoepitaxial film was also investigated. Prior to growth of the GaN:Mg films, a 0.7 μm thick Be-doped ($\sim 3\times 10^{19}\,cm^{-3}$) buffer layer followed by an undoped 0.2 μm GaN layer were deposited. The Be-doped layer helped to insure electrical isolation of the Mg-doped GaN layers [7]. Further details of the growth are provided elsewhere [8].

Several electrical and structural characterization techniques were also employed. Room-temperature Hall effect on a representative GaN homoepitaxial layer with [Mg] of $2\times 10^{19}\,cm^{-3}$ revealed a hole concentration of $\sim 10^{18}\,cm^{-3}$ with a mobility of $11\,cm^2/(V\,s)$. In addition to Mg depth profiles, SIMS revealed O levels of $\sim 6\times 10^{16}\,cm^{-3}$ and Si below the detection limit of $5\times 10^{14}\,cm^{-3}$; common residual SD impurities found in both MOCVD- and MBE-grown GaN. Atomic force microscopy showed typical rms surface roughness values of 5–10 Å. Finally, plan-view transmission electron microscopy performed on the GaN homoepitaxial layer with [Mg] of $1\times 10^{17}\,cm^{-3}$ revealed threading dislocation densities $\leqslant 5\times 10^{6}\,cm^{-2}$ over 5 μm × 5 μm areas.

The high-resolution PL at the GaN bandedge was excited by the 325 nm line of a HeCd laser and analyzed by 0.85 m double-grating spectrometer. The near bandedge and deep visible PL (2.0–3.3 eV) was generated by the 351 nm line of an Ar^+ laser and analyzed by a 0.25 m double-grating spectrometer. In both cases, the emission was detected by GaAs PMT detectors. The ODMR was performed at 24 GHz with the samples rotated in the (1 1 2 0) plane to obtain symmetry information. An UV-blocking filter was placed in front of the Si photodiode employed in the ODMR.

3. Results and discussion

The bandedge PL at 5 K from the two lowest Mg-doped GaN homoepitaxial layers and from the undoped GaN sample is shown in Fig. 1. The dominant emission (labeled $O^{\circ}X_A$) observed from the undoped reference GaN film at 3.472 eV is due to annihilation of excitons (involving holes from valence band A) bound to shallow O donors based on previous work [9]. This feature is also observed in the GaN:Mg layers and is consistent with the SIMS results that show O as the dominant residual SD species in these layers. The additional line (labeled $Mg^{\circ}X$) observed at 3.467 eV

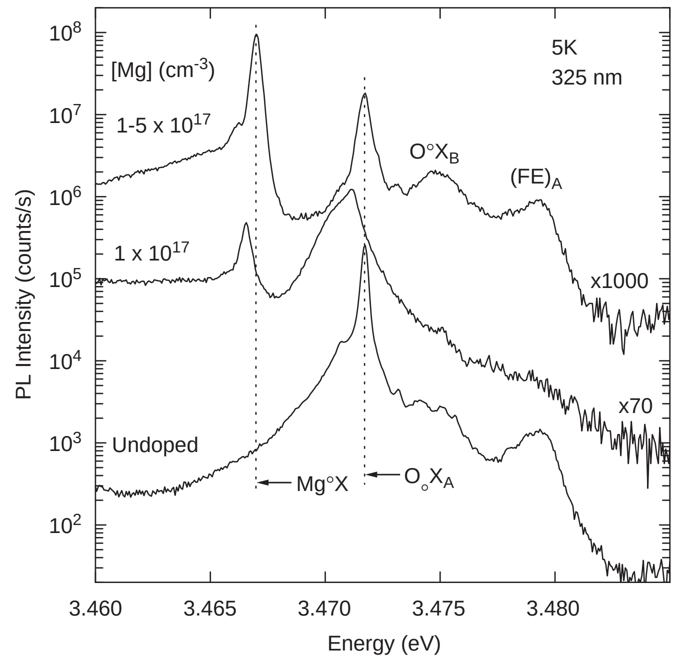

Fig. 1. High-resolution PL at 5 K in the bandgap region from two Mg-doped GaN homoepitaxial films and one undoped GaN homoepitaxial reference layer. The spectra are displaced vertically for clarity.

from the two Mg-doped GaN films is attributed to recombination of excitons bound to neutral shallow Mg acceptors. Its narrow linewidth of 0.2–0.4 meV indicates the high crystalline quality of these samples. This feature is similar to that previously reported by Stepniewski et al. [10] for MOCVD-grown Mg-doped GaN homoepitaxial layers deposited on GaN bulk crystals. We note that the small energy shifts (<0.5 meV) for the $O^{\circ}X_A$ and $Mg^{\circ}X$ PL lines from these GaN:Mg layers are likely due to slight differences in residual strain.

The PL < 3.3 eV observed at 2 K from several GaN homoepitaxial films with Mg-doping levels of 10^{17}–$10^{20}\,cm^{-3}$ is shown in Fig. 2. In contrast to many previous reports in literature for MBE- and MOCVD-grown Mg-doped GaN heteroepitaxial layers with $[Mg]\geqslant 3\times 10^{18}\,cm^{-3}$, no evidence was found for the so-called broad "blue" emission band with energy between 2.8 and 3.2 eV. Instead, all samples exhibited strong SD–SA recombination with zero phonon line at $\sim$3.27 eV and a series of LO phonon replicas. We note the pronounced narrowing of this emission from the samples with Mg doping near $1\times 10^{17}\,cm^{-3}$. This behavior is attributed to both the reduced threading dislocation density and Mg impurity concentration. The additional partially resolved feature approximately 33 meV below the 3.27 eV SD–SA ZPL (and LO phonon replicas) for the two lowest Mg-doped samples is similar to that first observed by Dingle and Ilegems [11] in undoped (n-type) GaN samples. It was suggested to be due to a second SD–SA recombination system. Finally, we also note (not shown) the absence of other visible PL bands between 1.8 and 2.8 eV in these samples.

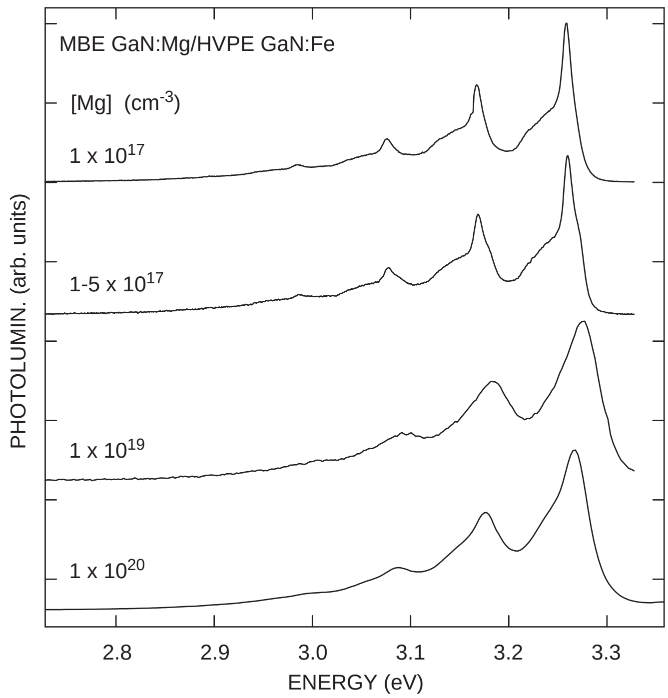

Fig. 2. PL<3.4 eV found at 2 K from several Mg-doped GaN homoepitaxial layers.

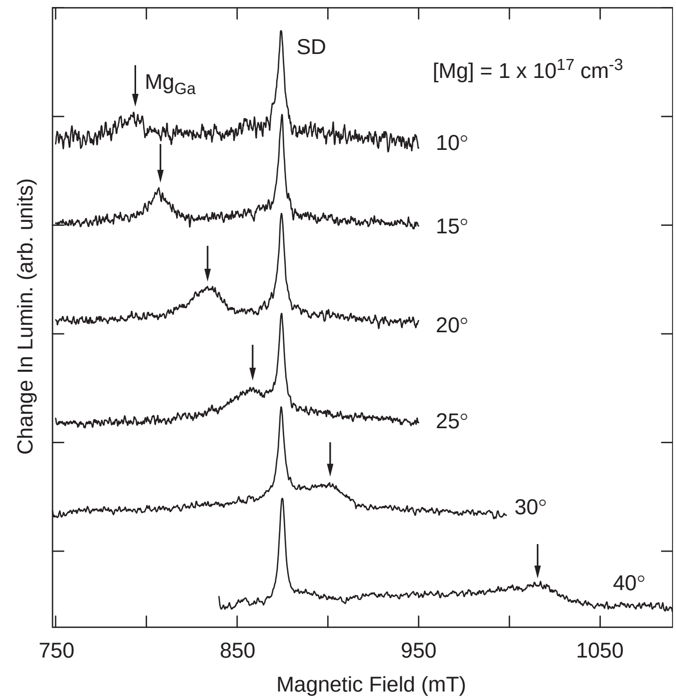

Fig. 3. ODMR spectra at 24 GHz observed on the 3.27 eV SD–SA PL from a homoepitaxial GaN layer doped with [Mg] of $1 \times 10^{17}\,cm^{-3}$ for several orientations of B with respect to the c-axis (microwave modulation frequency = 3 kHz).

Optically detected magnetic resonance obtained on the 3.27 eV SD–SA PL from the GaN homoepitaxial layer with $[Mg] = 1 \times 10^{17}\,cm^{-3}$ for several orientations of the magnetic field (**B**) with respect to the c-axis is shown in Fig. 3. Two luminescence-increasing signals are found. The first (labeled SD) is sharp (FWHM ~3.5 mT) with $g_{\parallel}$, $g_{\perp}$~1.950 and is a signature of effective-mass SD in GaN [2]. It is assigned to residual O SD on the N sites from the high-resolution PL and SIMS measurements.

The second feature (labeled Mg_{Ga}) is broader (FWHM~20 mT for angles$\leqslant$25°), is weakly observed for **B** within 10° of the c-axis and, most notably, shifts rapidly to higher field as **B** is rotated away from the c-axis (especially for angles >20°). In addition, a noticeable asymmetric broadening to the low-field side of this peak is observed for angles $\geqslant$25°. A plot of the g-values (triangles) of this resonance as a function of the angle (θ) between **B** and the c-axis is shown in Fig. 4. A fit to this data was made with the usual expression for g-tensors in the case of axial symmetry: $g(\theta) = (g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta)^{1/2}$, where $g_{\parallel}$ and $g_{\perp}$ are the g-values with **B** parallel and perpendicular to the c-axis, respectively. A good fit is found with $g_{\parallel} = 2.19 \pm 0.01$ and $g_{\perp}$~0. This highly anisotropic g-tensor is predicted from effective mass theory [4] for shallow Mg acceptors in wz-GaN where the ground state, from symmetry arguments, reflects the character of the $J = 3/2$, $m_J = \pm 3/2$ valence band edge. This previously elusive result via magnetic resonance techniques is attributed to the much reduced threading dislocation density and Mg impurity concentration compared to those typically found in the widely investigated Mg-doped GaN heteroepitaxial

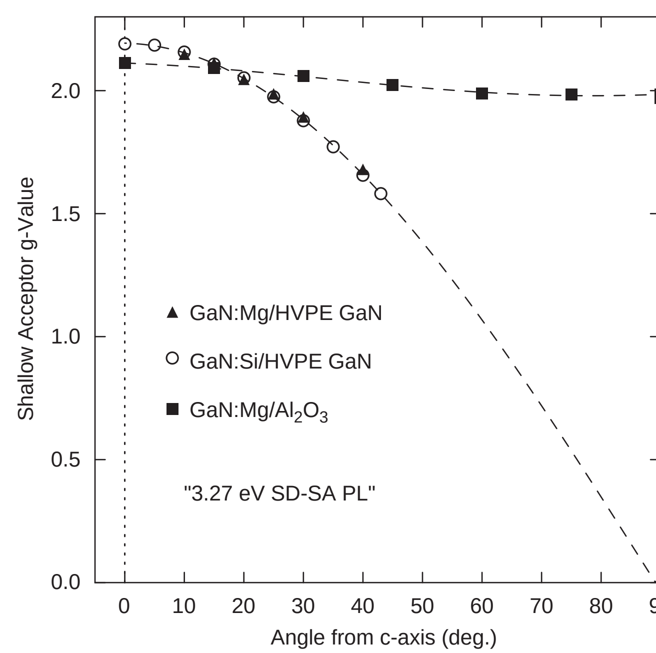

Fig. 4. The g-values of ODMR feature Mg_{Ga} in this work (triangles) and those reported previously for shallow acceptors in Si-doped GaN homoepitaxial layers (circles) and for Mg shallow acceptors in Mg-doped GaN heteroepitaxial films (squares). Dashed curves are fits to the data as described in the text.

layers. This is demonstrated explicitly in Fig. 4 by the nearly isotropic g-values (squares) observed for the shallow Mg acceptors via ODMR on the 3.27 eV SD–SA PL from a GaN heteroepitaxial layer with Mg-doping level of

$3\times10^{18}\,cm^{-3}$ grown on Al_2O_3 [12]. We note that ODMR was not found on the 3.27 eV SD–SA recombination from the GaN homoepitaxal films with Mg doping $\geqslant 10^{19}\,cm^{-3}$. We attribute this to the small average donor–acceptor pair separation (e.g.,$\sim$30 Å for [Mg] of $10^{19}\,cm^{-3}$ compared to $\sim$130 Å for [Mg] of $10^{17}\,cm^{-3}$) in such samples that result in recombination lifetimes that are too fast to alter spin populations for the microwave powers ($\sim$50 mW) available in these ODMR experiments.

Finally, ODMR was recently reported for the SA involved in the 3.27 eV SD–SA PL from a GaN homoepitaxial layer intentionally doped with Si ($2\times10^{17}\,cm^{-3}$) [13]. Si-doping studies as described by Murthy et al. [14] strongly indicated that the SA were due to some fraction of the Si impurities on the N host lattice sites. Most noteworthy, in addition to the similar excitonic emission energies of $\sim$3.467 eV, the magnetic resonance characteristics of this feature (including the highly anisotropic g-tensor as shown by the circles in Fig. 4 and the asymmetric broadening behavior observed with B rotated $\geqslant 25^\circ$ from the c-axis) are nearly identical with those found in this work for the Mg SA on the Ga sites.

4. Summary

PL and ODMR have been performed on several GaN homoepitaxial layers doped with Mg from 10^{17} to $10^{20}\,cm^{-3}$. In addition to strong emission at $\sim$3.467 eV attributed to annihilation of excitons bound to shallow Mg acceptors, each sample exhibited SD–SA recombination at 3.27 eV with no evidence for other deep visible PL bands. ODMR on this emission from the lowest Mg-doped sample revealed the first evidence for the highly anisotropic g-tensor predicted for effective-mass Mg acceptors in wz-GaN. Surprisingly, the characteristics of this feature are very similar to those found recently from ODMR of Si SA on the Ga host lattice sites.

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